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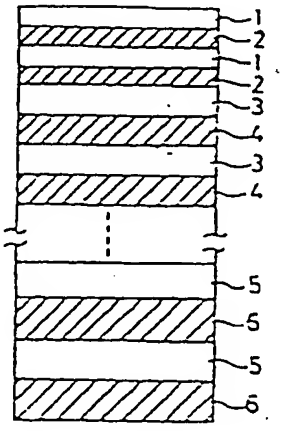
(54) [Title of the Invention]
Diffraction Grating

(57) [Summary]

[Objective] A difraction grating being able to diffract the light over a wide range of wavelengths is prepared by stacking more than two types of films of different indexes of refraction and by varying thicknesses of these films.

[Structure] A structure is made in such a manner that layers from materials of relatively diffrent indexes of refraction 1,3,5 and 2,4,6 are alternately stacked in an order of high , low indexes of refraction. One is able to cover a range of the diffraction wavelengths, say for example a range of 800- 2000 nm , by varying thicknesses of these constituent layers. In this case, one can obtain a good heat - rays reflective film which is able to refract the heat- rays when a visible light is passed through. This heat- rays reflective film can be used for the windows of cars, and buildings . One therefore is able to reduce the temperature increase inside the cars and the buildings .



1: Film of high index of refraction
0.4 μm thick
2: Film of low index of refraction
0.4 μm thick
3: Film of high index of refraction
0.41 μm thick
4: film of low index of refraction
0.41 μm thick
5: Film of high index of refraction
1.00 μm thick
6: Film of low index of refraction
1.00 μm thick

[Scope Covered in The Invention]

We claim :

{Claim 1]
A difraction grating which is characterized in that said diffraction grating is able to diffract the light over a wide range of wavelengths and is prepared by alternately stacking more than two types of films of relatively different indexes of refraction;

Claim 2]
The diffraction grating as set forth in claim (1) is characterized in that in said diffraction grating , thicknesses of the constituent layers are different for the set of different high, low indexes of refraction;

[Claim 3]
The diffraction grating as set forth in claim s (1) and (2) is characterized in that it is formed by alternately stacking more than two of films or sheets of different indexes of refraction;

[Claim 4]
The diffraction grating as set forth in claims (1) and (2) is characterized in that the stacking is carried out by coating each individual layer on top of one another;

[Claim 5]
The diffraction grating as set forth in claim s (1) through (4) is characterized in that thickness of each layer is varied by means of a mechanical procedure such as the extrusion method , press method and the like;

[Claim 6]
The diffraction grating as set forth in claims (1) through (5) is characterized in that said diffraction grating is constructed as a heat- rays reflective film .

[Detailed Description of the Invention]
[0001]
[Industrial Applications]

This invention relates to a diffraction grating . In particulalr, this invention is about a diffraction grating which is used in the applications where a wide range of wavelengths is diffracted such as the heat- rays reflective film.

[0002]
{Prior Art]

Conventionally, the Bragg diffraction grating has been known as the common diffraction grating. This diffraction grating is formed by recording interference fringes of light on a layer of for example photopolymer, gelatine chromate and silver salt. This grating , however has a narrow diffraction wavelength range, and a large range of diffraction wavelengths can not be covered with this type of diffraction grating.

[0003]

When this type of diffraction grating is employed in the applications of for example heat -rays reflective film, it is necessary that the diffraction wavelengths be in the range of more than a few hundreds nanometers.

[0004]
[Problems To Be Solved]

In an intention to solve the above problems, the objective of this invention is to provide a diffraction grating which is able to diffract light over a wide range of wavelengths and the grating is formed by stacking at least two layers of different indexes of refraction and by varying thicknesses of the constituent layers .

[0005]
[Procedures To Solve the Problems]

Generally, the lattice spacing pitch d and the diffraction wavelength wavelength λ are related to the incident angle θ by the relation of $2d\sin\theta = n\lambda$ ($n = 1,2,3,...$). Accordingly, a diffraction garting is constructed by stacking alternately a layer of high index of refraction and a layer of low index of refraction. In this case, variation is made in such a way that the lattice spacing pitch d would be different at the layer interval, one is able to

diffract light of various wavelengths. And one is able to widen the range of the diffraction wavelengths in the diffraction grating.

[0006]

We will describe a concrete example . As shown in Fig. 1, for example, film 1 of a high index of refraction of a thickness of 0.40 μm, film 3 of a high index of refraction of a thickness of 0.41 μm, ...film 5 of a high index of refraction with a thickness of 1.00 μm; and films 2,4, ... 6 of low index of refraction and of the same thicknesses are alternately stacked to form a diffraction grating. With regard to the layers of specific thicknesses , number of the layers in this stack is 4 in this case. However, the diffraction grating can be constructed with any number of layers and will not therefore be limited by this particular number .

[0007]

In this diffraction grating as shown in Fig. 2, light of a wavelength of 800 nm is diffracted with a perpendicular incidence in the layer of the first thickness. With the layers of the orderly increasing thicknesses , light of a wavelengths of 820 nm, ..., 2000 nm are respectively diffracted, As a result , light of a wide range of wavelengths of 800 - 2000 nm is diffracted.

[0008]

Procurement and stacking of the films of the orderly varying thicknesses are not easy. In practice, films of thicknesses of several times or few tens times of the above-mentioned thicknesses are used in the stacking . Afterwards, thicknesses of the layers are reduced by using the mechanical methods such as the extrusion method or the press method. It is also conceivable that each layer of a specific thickness is formed by coating; and a desired stack can be formed by orderly repeating the coating of these layers. Morever, a combination of the aforementioned mechanical methods and the coating method is possible. Materials of high indexes of refraction and materials of low indexes of refraction do not have to be limited to one type of material. One can combine different materials of high indexes of refraction with materials of low indexes of refraction. Furthermore, it is plausible even when variation in the thicknesses of the layers is made by orderly increasing thicknesses from one surface of the stack to the other surface of the stack ; or even when layers of different thicknesses are

distributed randomly. There is not therefore any particular limitation for this variation.

[0009]

The following materials can be used for the materials of high indexes of refraction and those of low indexes of refraction. These materials can be stacked in any possible ways. In the following, indexes of refraction in the d line are also shown.

[0010]

Polyvinylidene fluoride	1.42
Polydimethylsylilene (polydimethylsiloxane)	1.43
Polytrifluoroethylmethacrylate	1.437
Polyoxypropylene	1.4495
Polyvinylisobutylether	1.4507
Polyvinylethylether	1.4540
Polyoxyethylene	1.4563
Polyvinylbutylether	1.4563
Polyvinylpentylether	1.4581
Polyvinylhexylether	1.4591
Poly (4-methyl- 1- pentene)	1.459- 1.465
Celluloseacetate butyrate	1.46- 1.49
Poly (4-fluoro-2- trifluoromethylstyrene)	1.46
Polyvinyloctylether	1.4613
Poly (vinyl 2- ethylhexylether)	1.4626
Polyvinyldecylether	1.4628
Poly (2-methoxyethylacrylate)	1.463
Polybutylacrylate	1.4631
Polybutylacrylate	1.466
Poly (t-butylmethacrylate)	1.4638
Polyvinyldodecylether	1.4640
Poly (3-ethoxypropylacrylate)	1.465
Polyoxycarbonyltetramethylene	1.465
Polyvinylpropionate	1.4665
Polyvinylacetate	1.4665
Polyvinylmethylether	1.467
Polyethylacrylate	1.4685
Ethylene- vinylacetate copolymer	1.47- 1.50

(80%- 20% vinylacetate)	
Cellulosepropionate	1.47- 1.49
Celluloseacetatepropionate	1.47
Benzylcellulose	1.47- 1.58
Phenol formaldehyd resin	1.47- 1.50
Cellulosetriacetate	1.47- 1.48
Polyvinylmethylether (isotactic)	1.4700
Poly(3-methoxypropylacrylate)	1.471
Poly (2-ethoxyethylacrylate)	1.471
Polymethylacrylate	1.472- 1.480
Polyisopropylmethacrylate	1.4728
Poly (1-decene)	1.4730
Polypropylene (atactic, density 0.8575 g/cm3)	1.4735
Poly(vinylsec-butylether) (isotactic)	1.4740
Polydodecylmethacrylate	1.4740
Polyoxyethyleneoxysuccinoyl (polyethylenesuccinate)	1.4744
Polytetradecylmethacrylate	1.4746
Ethylene-propylene copolymer (EPR -rubber)	1.4748- 1.48
Polyhexadecylmethacrylate	1.4750
Polyvinylformate	1.4757
Poly(2-fluoroethylmethacrylate)	1.4768
Polyisobutylmethacrylate	1.477
Ethylcellulose	1.479
Polyvinylacetal	1.48- 1.50
Celluloseacetate	1.48- 1.50
Cellulosetripropionate	1.48- 1.49
Polyoxymethylene	1.48
Polyvinylbutyral	1.48- 1.49
Poly (n-hexylmethacrylate)	1.4813
Poly (n-butylmethacrylate)	1.483
Polyethylidenemethacrylate	1.4831
Poly (2-ethoxyethylmethacrylate)	1.4833
Polyoxyethyleneoxymaleoil (polyethylenemalate)	1.4840
Poly(n- propylmethacrylate)	1.484
Poly (3,3,5-trimethylcyclohexyl methacrylate)	1.485
Polyethylmethacrylate	1.485
Poly (2-nitro-2-methylpropylmethacrylate)	1.4868
Polytriethylcarbninylmethacrylate)	1.4889

Poly (1,1-diethylpropylmethacrylate)	1.4889
Polymethylmethacrylate	1.4893
	1.490
Poly (2-decyl-1, 3-butadiene)	1.4899
Polyvinylalcohol	1.49- 1.53
Polyethylglycolate methacrylate	1.4903
Poly (3-methylcyclohexylmethacrylate)	1.4947
Poly (cyclohexyl α-ethoxyacrylate)	1.4969
Methylcellulose (low viscosity)	1.497
Poly (4-methylcyclohexylmethacrylate)	1.4975
Polydecamethylene glycoldimethacrylate	1.4990
Polyurethane	1.5- 1.6
Poly (1,2- butadiene)	1.5000
Polyvinylformal	1.50
Poly (2-bromo-4-trifluoromethylstyrene)	1.5
Cellulose nitrate	1.50 - 1.514
Poly (sec-butyl α-chloroacrylate)	1.500
Poly (2-heptyl-1, 3-butadiene)	1.500
Poly (ethyl α- chloroacrylate)	1.502
Poly(2-isopropyl-1, 3 butadiene)	1.5028
Poly (2- methylcyclohexylmethacrylate)	1.5028
Polypropylene (density 0.9075 g/cm3)	1.5030
Polyisobutene	1.505- 1.51
Polybornylmethacrylate	1.5059
Poly (2-t-butyl-1, 3-butadiene)	1.5060
Polyethyleneglycol dimethacrylate	1.5063
Polycyclohexylmethacrylate	1.5066
Poly (cyclohexane diol-1,4-dimethacrylate)	1.5067
Butyl rubber (non-vulcanization)	1.508
Polytetrahydrofurfurylmethacrylate)	1.5096
Gutta-percha (β)	1.509
Polyethylene ionomer	1.51
Polyoxyethylene (high molecular weight)	1.51- 1.54
Polyethylene (density 0.914 g/cm3)	1.51
(density 0.94-0.945 g/cm3)	1.52-1.53
(density 0.965 g/cm3)	1.545
Poly (1-methylcyclohexylmethacrylate)	1.5111
Poly (2-hydroxyethylmethacrylate)	1.5119
Polyvinylchloroacetate	1.512
Polybutene (isotatic)	1.5125

Polyvinylmethacrylate	1.5129
Poly (N-butyl-methacrylamide)	1.5135
Gutta-percha (α)	1.514
Terpene resin	1.515
Poly (1,3- butadiene)	1.5154
Shellac	1.51- 1.53
Poly (methyl α- chloroacrylate)	1.517
Poly (2-chloroethylmethacrylate)	1.517
Poly (2-diethylaminoethylmethacrylate)	1.5174
Poly (2-chlorocyclohexylmethacrylate)	1.5179
Poly (1,3-butadiene) (35% cis;56% trans ;7% 1,2- contet)	1.5180
Natural rubber	1.519- 1.52
Polyallylmethacrylate	1.5196
Polyvinylchloride + 40% dioctylphthatate	1.52
Polyacrylonitrile	1.52 1.5187
Polymethacrylonitrile	1.52
Poly (11,3-butadiene) (sic type rich)	1.52
Butadiene- acrylonitrile copolymer	1.52
Polymethylisopropenylketone	1.5200
Polyisoprene	1.521
Polyester resin rigid (about 50% styrene)	1.523- 1.54
Poly (N-(2- methoxyethyl) methacrylamide	1.5246
Poly (2,3- dimethylbutadiene) (methyl rubber)	1.525
Vinylchloride -vinylacetate copolymer (95/5-90/10)	1.525-1.535
Polyacrylic acid	1.527
Poly(1,3 -dichloropropylmethacrylate)	1.5270
Poly (2-chloro- 1- (chloromethyl) ethylmethacrylate)	1.5270
Polyacrolein	1.529
Poly (1-vinyl-2-pyrrolidone)	1.53
Hydrochlorate rubber	1.53- 1.55
Nylon 6; nylon 6,6; nylon 6,10 (plastic form) (nylon -6-fiber : 1.515 transverse direction 1.565 fiber direction)	1.53
Butadiene-styrene copolymer (about 30% styrene) block copolymer	1.53
Poly (cyclohexyl α-chloroacrylate)	1.532
Poly (2-chloroethyl α-chloroacrylate)	1.533
Butadiene -styrene copolymer (about 75/25)	1.535
Poly (2-aminoethylmethacrylate)	1.537

Polyfurfurylmethacrylate	1.5381
Protein	1.539- 1.541
Polybutylmercapthylmethacrylate	1.5390
Poly (1-phenyl-n-amylmethacrylate)	1.5396
Poly (N-methyl- methacrylamide)	1.5398
Cellulose	1.54
Polyvinylchloride	1.54- 1.55
Ureaformaldehyd resin	1.54- 1.56
Poly (sec-butyl α-bromoacrylate)	1.542
Poly (cyclohexyl α-bromoacrylate)	1.542
Poly (2-bromoethylmethacrylate)	1.5426
Polydihydroabietic acid	1.544
Polyabietic acid	1.546
Polyethylmercapthyl methacrylate	1.547
Poly (N-allylmethacrylamide)	1.5476
Poly (1-phenylethylmethacrylate)	1.5487
Polyvinylfuran	1.55
Poly (2-vinyltetrahydrofuran)	1.55
Poly (vinylchloride) +40% tricrezylphosphate	1.55
Epoxy resin	1.55-1.60
Poly (p-methoxybenzylmethacrylate)	1.552
Polyisopropyl methacrylate	1.552
Poly (p-isopropylstyrene)	1.554
Polychloroprene	1.554- 1.558
Poly (oxyethylene-α-benzoate-ω-methacrylate)	1.555
Poly (p,p'-xylenyldimethacrylate)	1.5559
Poly (1-phenylallyl methacrylate)	1.5573
Poly (p-cyclohexylphenylmethacrylate)	1.5575
Poly (2-phenylethylmethacrylate)	1.5592
Poly (oxycarbonynoxy-1, 4-phenylene-1-propyl -butylidene-1, 4-phenylene)	1.5602
Poly (1- (o-chlorophenyl)ethylmethacrylate)	1.5624
Styrene- maleic anhydride copolymer	1.564
Poly (1-phenylcyclohexylmethacrylate)	1.5645
Poly (oxycarbonynoxy-1, 4-phenylene-1, 3 -dimethyl- butylidene-1, 4-phenylene)	1.5671
Poly (methyl α- bromoacrylate)	1.5672
Polybenzylmethacrylate	1.5680
Poly (2- (phenylsulfonyl) ethylmethacrylate)	1.5682
Poly (m- crezylmethacrylate)	1.5683

Styrene- acrylonitrile copolymer (about 75/25)	1.57
Poly (oxycarbonyoxy- 1,4- phenyleneisobutylidene -1, 4-phenylene)	1.5702
Poly (o-methoxyphenylmethacrylate)	1.5705
Polyphenylmethacrylate	1.5706
Poly (o- crezylmethacrylate)	1.5707
Polydiallylphthalate	1.572
Poly (2,3- dibromopropylmethacrylate)	1.5739
Poly (oxycarbonyloxy-1, 4-phenylene-1-methyl -butylidene-1, 4-phenylene)	1.5745
Poly (oxy-2, 6-dimethylphenylene)	1.575
Polyoxyethyleneoxyterephthaloyl (amorphous) (polyethylene terephthalate) (crystalline fiber :1.51 in transverse direction 1.64 in the fiber direction)	1.5750
Polyvinylbenzoate	1.5775
Poly (oxycarbonyloxy-1, 4-phenylenebutylidene -1, 4-phenylene)	1.5792
Poly (1,2-diphenylethylmethacrylate)	1.5816
Poly (o- chlorobenzylmethacrylate)	1.5823
Poly (oxycarbonyloxy-1, 4-phenylene-sec-butylidene-1, 4-phenylene)	1.5827
Polyoxypentaerythritoloxy phthaloyl)	1.584
Poly (m-nitrobenzylmethacrylate)	1.5845
Poly (oxycarbonyloxy-1, 4-phenylene isopropylidene -1, 4- phenylene)	1.5850
Poly (N- (2-phenylethyl) methacrylamide)	1.5857
Poly (4-ethoxy-2 -methylstyrene)	1.5868
Poly (o-methylstyrene)	1.5874
Polystyrene	1.59- 1.592
Poly (oxycarbonyloxy-1, 4-phenylenecyclohexylidene -1, 4-phenylene)	1.5900
Poly (o- methoxystyrene)	1.5932
Polydiphenylmethylmethacrylate	1.5933
Poly (oxycarbonyloxy-1, 4-phenyleneethylidene -1, 4-phenylene)	1.5937
Poly (p-bromophenyl methacrylate)	1.5964
Poly (N-benzylmethacrylamide)	1.5965
Poly (p-methoxystyrene)	1.5967
Hardening rubber (32%S)	1.6

POlyvinylidene chloride	1.60- 1.63
Polysulfide ("Thiokol")	1.6- 1.7
Poly (o-chlorodiphenyl methylmethacrylate)	
Poly (oxycarbopnyloxy-11, 4-(2,6- dichloro) phenylene- isopropylidene-1,4- (2,6- dichloro)phenylene)	1.6056
Poly (oxycarbonyloxy bis (1, 4- (3, 5- dichlorophenylene)	1.6056
Polypentachlorophenylmethacrylate	1.608
Poly (o-chlorostyrene)	1.6098
Poly (phenyl α- bromoacrylate)	1.612
Poly (p-divinylbenzene)	1.6150
Poly (N-vinylphthalimide)	1.6200
Poly (2, 6-dichlorostyrene)	1.6248
Poly (β- naphthylmethacrylate)	1.6298
Poly (α- naphthyl carbinylmethacrylate)	1.63
Polysulfone	1.633
Poly (2- vinylthiophene)	1.6376
Poly (α- naphthylmethacrylate)	1.6410
Poly (oxycarbonyloxy-1, 4-phenylene diphenyl -methylene-1, 4-phenylene)	1.6539
Polyvinylphenylsulfide	1.6568
Butylphenolformaldehyd resin	1.66
Urea-thiourea- formaldehyd resin	1.660
Polyvinylnaphthalene	1.6818
Polyvinylcarbazol	1.683
Naphthalene- formaldehyd resin	1.696
Phenol- formaldehyd resin	1.70
Polypentabromophenylmethacrylate	1.71

[0011]

From the above explanation, it is clear that the diffraction grating of this invention is characterized in that it is formed by alternately stacking at least two materials of diffrent indexes of refraction ; one with a high index of refraction and the other with a low index of refraction.

[0012]

In this case, thicknesses of the layers are diffrent for the set of different high, low indexes of refraction to cover a wide range of wavelengths.

[0013]

In reality, for forming this type of diffraction grating, films or sheets from at least two materials of different indexes of refraction are alternately stacked. It is desirable that the stacking is made by coating each individual layer in the structure. Furthermore, to control the thickness of each layer, it is preferred that the thickness deformation be formed , using the mechanical procedure such as the extrusion method or the press method. This deformation is not applied only in the direction of thinning the thicknesses , but can also follow the direction of enlarging the thicknesses.

[0014]

This type of diffraction grating can be used for example as a heat- rays reflective film.

[0015]
[Effect]

In the present invention, structure of the diffraction grating is formed by stacking alternately the layers of relatively high indexes of refraction and layers of relatively low indexes of refraction. Accordingly, diffraction grating with a wide range of diffraction wavelengths can be obtained.

[0016]
[Examples]

In the following, we will describe one example of this invention. Polyvinylidene chloride film (25 μm thick, index of refraction of 1.62) and polyvinylidene fluoride film (25 μm thick, index of refraction of 1.42) were stretchingly treated in a hot air atmosphere , With respet to these materials, a total of 13 types of the folllowing thicknesses were used to form the film : 10 μm , 11, 25 μm , 12 μm , ... 23 μm , 75 μm , 25 μm .

[0017]

First of all, films of a thickness of 10 μm were respectively stacked in every four sheets to make a total of 8 sheets with indexes of refraction being in the order of high , low, high, low... While still heating, a dry lamination was carried out.

[0018]

Films of the thicknesses of 11, 25 μm, 12 μm, ..., 23, 75 μm , 25 μm were orderly used. Similarly, the lamination was carried out.

[0019]

The thus formed lamination with 13 layers was stretchingly treated. By extruding 25 times , the thickness will be reduced to 1/25 of their original value. The lamination with 13 layers which had been exposed to this kind of treatment is shown with their corresponding diffraction characteristics. As shown in Fig. 3, with the lamination of 13 layers , one was able to obtain a diffraction grating which has a smooth diffraction characteristic, covering a wide range of wavelengths from 800 nm to 2000 nm.

[0020]
[Effect of the Invention]

From the above explanation, it is clear that with an alternate stacking of materials of high and low indexes of refraction and of different thicknesses , one is able to prepare a diffraction grating which covers a wide range of wavelengths.

[0021]

To be concrete, with the diffraction grating proposed in this invention, one is able to cover a range of the diffraction wavelengths of 800 - 2000 nm. In this case, the grating can be used as a good heat-rays reflective film which reflects heat -rays when a visible light is passed through. This - rays reflective film can be used in the windows of the cars or buildings ; and increase in the temperature inside the cars and buildings can therefore be reduced.

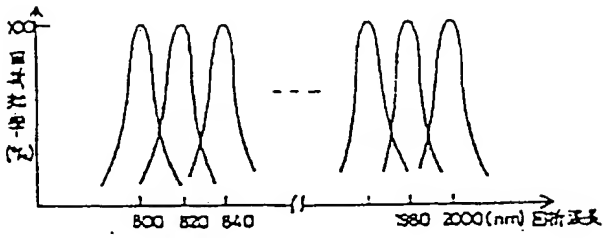
[Brief Description of Figures]

[Figure 1] shows a cross-sectional view of a concrete example of this invention.
[Fig.2] shows the diffraction characteristics of the diffraction grating in Fig. 1.
[Fig. 3] shows the diffraction characteristics of the diffraction grating of this example.
[Fig. 4] shows the diffraction characteristics of each lamination film in the example.

[LEGEND]

1,3,5.... High index of refraction film
22,4,6.... Low index of refraction film.

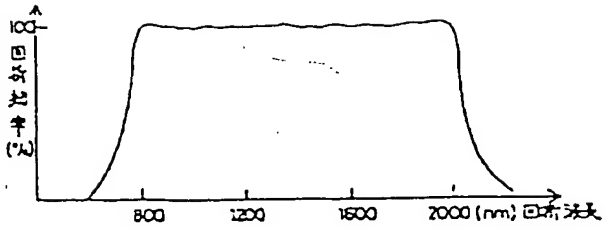
【図2】



Diffraction efficiency

Diffraction wavelength

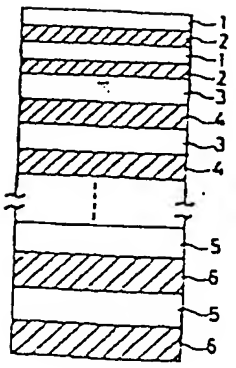
【図3】



Diffraction efficiency

Diffraction wavelength

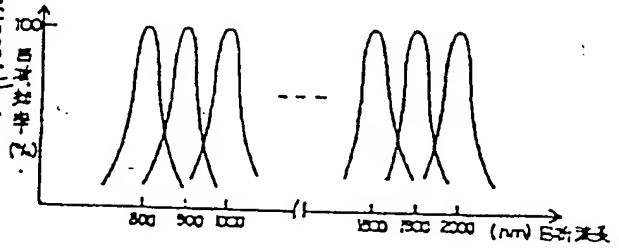
【図1】



1: Film of high index of refraction 0.4 μm thick
1：高屈折率フィルム0.4μm厚
2：低　〃　low
3：高屈折率フィルム0.41μm厚 high
4：低　〃　low
5：高屈折率フィルム1.00μm厚 high 1.00μm thick
6：低　〃

6: Film of low index of refraction, 1.00μm thick

【図4】



Diffraction efficiency

Diffraction wavelength